

### Method for treating metal surfaces by carboxylation

The invention relates to a method of depositing conversion coatings on a metal surface chosen from amongst zinc, iron, aluminium, copper, lead, and alloys thereof, as well as galvanised, aluminium-coated, copper-coated steels which make it possible to produce at high speed conversion coatings formed of very small crystals.

When they are applied before the shaping of the metal sheet, these conversion treatments for metal surfaces generally have at least one of the following effects:

- improvement in the properties of mechanical friction with lubrication, for example for the stamping of metal sheets,
- temporary protection against corrosion.

For this first type of application, treatments known as pre-phosphating are used more particularly which culminate in the deposition of a metal phosphate coating of which the weight per unit area is of the order of 1 to 1.5 g/m<sup>2</sup>.

However, these conversion treatments can also be carried out after the shaping of the metal sheet, in order to improve the adhesion of organic coatings deposited subsequently, such as paints. Mention will be made by way of example of the phosphating treatment which culminates in the deposition of a metal phosphate coating of which the weight per unit area is greater than that of a pre-phosphating treatment.

These different conversion treatments generally consist of anodic dissolution of the metal elements of the surface, followed by a precipitation on this surface of the compounds formed by the reaction of the dissolved metal elements with the constituents present in the conversion bath. The dissolution necessitates the creation of oxidising conditions in relation to the metal of the surface and generally takes place in an acid environment. The precipitation of the metal compounds in order to form the conversion coating necessitates a sufficiently high concentration and is favoured by an environment which has become less acid locally under the effect of the dissolution of the metal. It is the nature and the structure of the compounds

precipitated on the treated surface which determine the degree of protection against corrosion, of improvement in the tribological properties and/or properties of adhesion, as well as the other properties of the coating.

In order to ensure the superficial oxidation of the surface to be treated and to favour dissolution thereof, it is possible to proceed in a chemical or electrochemical manner: with the aid of a chemical agent for oxidation of the metal to be introduced into the treatment solution, and/or by electric polarisation of the surface whilst subjecting it to the action of the treatment solution.

Apart from a possible oxidising agent, the conversion baths essentially contains anions and cations which are capable of forming insoluble compounds with the dissolved metal of the surface. Thus the principal conversion treatments are treatments of chromating on zinc-coated or aluminium-coated steel, phosphating on non-alloyed uncoated steels or on coated steels, or oxalating on alloyed steels such as stainless steels for example.

After being placed in contact with a conversion bath, the treated surface is generally washed in order to eliminate the unreacted components of the surface and/or of the treatment solution, then this surface is dried in particular in order to harden the conversion coating and/or to improve the properties thereof.

The conditions of application, the nature and the concentration of the additives have a substantial influence on the structure, the morphology and the compactness of the conversion coating obtained, and therefore upon the properties thereof.

The conversion treatment can itself be preceded by a pre-treatment consisting generally of prior degreasing and washing of the surface followed by an operation known as refining with the aid of a pre-treatment solution adapted in order to create and/or to favour nucleation sites on the surface to be treated.

To this end sols or colloidal suspensions of titanium salts are currently used on zinc-coated surfaces, permitting a conversion coating to be obtained subsequently which has smaller crystals in a denser coating.

At the end of the conversion treatment it is also possible to effect a post-treatment in order to improve the properties of the conversion coating. Thus a chromating post-treatment may be effected on a conversion coating obtained by phosphating.

International Patent Application WO95/21277 describes an aqueous composition for treatment of zinc-coated surfaces comprising:

- a polyhydroxyaryl carboxylic acid, for example gallic acid or protocatechuic acid, or a depside of this acid which may result from reaction thereof with glucose, such as tannic acid, and
- a silane-based adhesion promoter.

Conventional accelerating agents for zinc-coated surfaces, such as phosphates, nitrates, fluorides or organic acids, are used with this treatment composition.

The treatment effected with the aid of this composition affords not only a good protection against corrosion but also good adhesion for paints.

Patent Application FR 2 465 008 describes a method of depositing conversion coatings on zinc-coated surfaces with the aid of a treatment solution which may contain a soluble oxalate, associated with activating agents which are carboxylic acids, particularly short diacids.

The concentration of oxalic acid in the treatment solutions described is less than 7.5 g/l, or 0.08 mole/litre.

The document EP 0 494 431 (KAWASAKI) teaches that the addition of a carboxylic acid to chromating treatment solutions containing colloidal silica makes it possible to improve the

properties of the conversion coatings obtained on zinc-coated surfaces and/or permits a substantial reduction in the chromium content of these solutions.

The weight of the coating, or weight per unit area, resulting from these different treatments is very variable depending upon the principal objective and may range from less than 1 g/m<sup>2</sup> to 8 g/m<sup>2</sup>.

The different treatments according to the prior art, such as the chromating, phosphating and oxalating treatments, exhibit a major drawback which is the toxicity of these products for humans and for the environment in general. Furthermore, when metal sheets bearing such conversion coatings are spot-welded this creates emissions of toxic fumes.

Therefore the object of the invention is to offer a conversion treatment for metal surfaces before they are shaped, with the aid of a bath which is free of compounds which are harmful to the environment but also making it possible to deposit on these surfaces conversion coatings which are more effective in order to protect against corrosion and/or for pre-lubrication than those obtained by the methods according to the prior art.

Another object of the invention is also to be able to apply an organic coating with a good adhesion, particularly by cataphoresis, to a surface treated according to the invention after it has been shaped and degreased, which presupposes that the applied conversion coating is eliminated easily at the time of this degreasing.

To this end, the invention relates to a method of treatment by carboxylation, before shaping, of a metal surface chosen from amongst zinc, iron, aluminium, copper, lead, and alloys thereof as well as galvanised, aluminium-coated, copper-coated steels, in oxidising conditions in relation to the metal, by bringing the said metal surface into contact with an organic or hydro-organic aqueous bath comprising at least one organic acid in free form or in the form of salt, characterised in that:

- the said organic acid is a saturated or unsaturated aliphatic monocarboxylic or dicarboxylic acid,
- the said organic acid is in solution and/or in emulsion in the bath at a concentration greater than 0.1 mole/litre,
- the pH of the bath is acidic.

The invention also relates to the use of the said method of surface treatment by carboxylation for the temporary protection of the said metal surface against corrosion.

The invention further relates to a method of producing a shaped metal sheet having a metal surface chosen from amongst zinc, iron, aluminium, copper, lead, and alloys thereof, as well as galvanised, aluminium-coated, copper-coated steels, in which a surface treatment of the said metal sheet is carried out according to the invention, the said treated metal sheet is oiled and it is shaped. It is preferable more particularly to apply this method according to the invention to a sheet of steel coated with zinc or zinc alloy which is then shaped by stamping.

The invention will be better understood upon reading the following description which is given by way of non-limiting example with reference to the accompanying drawings, in which:

- Figure 1 illustrates the evaluation of the behaviour on stamping of sheets not treated according to the invention and oiled (symbol  $\diamond$ ) and sheets treated according to the invention and not oiled (symbol  $\Delta$ ) or oiled (symbol  $\square$ ); it represents the evolution of the maximum stamping force  $F_{\max}$  as a function of the blank holder force  $F_s$ .
- Figure 2 represents the evolution of the weight per unit area  $P$  of the conversion coating obtained according to the invention as a function of the duration of immersion  $D_1$  in a carboxylation solution, using a chemical means of oxidation of the zinc and the following co-solvents:
  - ethanol (symbol +),
  - n-propanol (symbol x),

- dimethyl sulphoxide (DMSO, symbol  $\Delta$ ),
- N-methyl-2-pyrrolidone (NMP, symbol  $\square$ ),
- diacetone alcohol (DAA, symbol  $\circ$ ).

- Figure 3 concerns the embodiment of the method according to the invention in which an electrochemical means is used for oxidation of the zinc, and shows for two different current densities (symbol  $\square = 10 \text{ mA/cm}^2$  - symbol  $\Delta = 25 \text{ mA/cm}^2$ ) the evolution of the weight per unit area P of the conversion coating obtained as a function of the duration of immersion Dc in the carboxylation solution.

- Figure 4 illustrates a potentiometric evaluation of the resistance to aqueous corrosion, in terms of polarisation resistance Rp as a function of the immersion time in the measurement electrolyte, for the following surfaces:

- untreated ("bare") zinc-coated surface, represented by the symbols +,
- zinc-coated surface treated by carboxylation according to the invention without post-treatment with:
  - heptanoic acid (symbol  $\Delta$ ),
  - decanoic acid (symbol x),
  - a mixture of heptanoic and decanoic acids (symbol \*),
- zinc-coated surface treated by carboxylation with heptanoic acid, and with post-treatment with the aid of a solution containing rare earth metals: symbol  $\square$  for Gd, symbol  $\diamond$  for Lu.

According to the invention conversion coatings are deposited by carboxylation of metal surfaces by bringing the surface into contact with an organic or hydro-organic aqueous bath comprising at least one organic acid in solution or in emulsion, in oxidising conditions in relation to the metal.

The present invention used aliphatic monocarboxylic or dicarboxylic acids, possibly having one or several unsaturations.

The acidity constants of the acids being of the order of 4.8, the natural pH of the baths according to the invention will generally be lower than this value. If it is wished to lower the pH, the treatment bath can be acidified, for example with the aid of nitric acid. The pH of the bath could also be increased by adding soda, for example. The acid bath used in the treatment according to the invention must in all cases have a pH value between 1 and 7, the upper limit making it possible to avoid the presence of a metal hydroxide in the conversion coating. As to the minimum value of the pH, this will be adapted as a function of the metal of the surface in order to ensure satisfactory deposition of the conversion coating.

The at least one organic acid used according to the invention is put in solution or in emulsion in the bath at a concentration greater than 0.1 mole/litre.

If the concentration of organic acid in the treatment bath is lower than 0.1 mole/litre, the speed of formation of the conversion coating based on metal carboxylate is no longer sufficient to obtain a conversion coating which is effective in the time allowed for the treatment.

In a preferred embodiment, the aliphatic organic acids according to the present invention are chosen from amongst the saturated monocarboxylic acids having from 5 to 16 carbon atoms. Hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid and decanoic acid are more particularly preferred.

In another preferred embodiment, the aliphatic organic acids according to the present invention are chosen from amongst the unsaturated monocarboxylic acids having from 10 to 18 carbon atoms. Undecenoic acid, oleic acid or linoleic acid are more particularly preferred.

In another preferred mode of embodiment, the aliphatic organic acids according to the present invention are chosen from amongst the saturated dicarboxylic acids having from 4 to 12 carbon atoms. Sebacic acid or azelaic acid are more particularly preferred.

In another preferred embodiment, the at least one aliphatic monocarboxylic acid retained is heptanoic acid.

More preferably, the bath comprises, in addition to heptanoic acid, decanoic acid or undecenoic acid.

Due to the use of a mixture of organic acids, such as heptanoic acid and decanoic acid or undecenoic acid, a conversion coating is obtained which is much denser and more effective in order to protect the metal surface against corrosion.

The oxidising conditions of the carboxylation bath are obtained by the following means:

- either by an addition to the bath of a chemical agent for oxidation of the metal adapted to the nature thereof, such as perborate tetrahydrate or hydrogen peroxide,
- or by causing an electric current to circulate between the metal surface previously immersed in the bath and at least one backing electrode, likewise immersed.

In the case where the oxidising conditions in relation to zinc are obtained by addition to the bath of a chemical agent for oxidation of zinc, this oxidising agent and/or accelerator is preferably chosen from amongst the group comprising sodium perborate, nitrites, hydrogen peroxide, hydroxylamine sulphate and nitroguanidine.

The conversion baths may optionally contain:

- agents for regulation of the pH or buffer agents in order to regulate the conditions of formation of the conversion coating on the surface,
- additives which facilitate the implementation of the treatment and the distribution of the bath over the surface to be treated, such as surfactants,
- additives which permit the service life of the bath to be increased, such as for example chelating agents in order to delay the precipitation of compounds other than those which it is wished to obtain in the conversion coating, or bactericidal agents, and
- agents for accelerating the treatment.



The conversion treatment bath according to the invention may also comprise a co-solvent such as ethanol, n-propanol, butanol, dimethylsulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP), 4-hydroxy-4-methyl-2-pentanone, diacetone alcohol, ethers of glycol, etc., or other organic acids or minerals. Diacetone alcohol is more particularly preferred.

A surprising result was obtained when the carboxylation treatment bath comprises a solution of rare earth ions such as gadolinium in the +3 oxidation state at a concentration greater than or equal to  $1.10^{-3}$  mole/litre.

The conversion coating obtained is then composed of two types of crystals of different composition and possibly of different shape, and it is even more effective for the resistance to corrosion.

Preferably the concentration of organic acids in the bath, the conditions of use of this bath and the oxidising conditions in relation to the metal are adapted to obtain on the metal surface a carboxylation coating with a weight per unit area of between 1 and 6 g/m<sup>2</sup>.

Other advantages of the method according to the invention will become apparent upon reading the non-limiting examples of the present invention which are presented below.

#### **MATERIALS for obtaining the conversion coatings:**

##### **1) Characteristics of the substrates tested**

Steel sheet of ES quality (steel for stamping) or of HES quality (steel for deep drawing), micro-alloyed or not, having a thickness of between 0.7 and 1.2 mm, bare or covered with a coating of zinc with a thickness of approximately 10 µm, applied by electrodeposition in a bath based on chlorides or sulphates, or by hot galvanisation.

##### **2) Components of the conversion treatment baths tested**

2.a - Solvent and co-solvent(s)

The treatment solutions tested are generally based on water as principal solvent and ethanol as co-solvent; propanol, DMSO, NMP or 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) or other polar solvents at least partially miscible in water can also be used as co-solvents.

2.b - Organic acid

For the examples illustrating the invention, this is heptanoic acid (abbreviation: HC<sub>7</sub>, product Aldrich, reference 25,873-3) and/or decanoic acid (abbreviation HC<sub>10</sub>, product Rectapur, reference 20 243.298, sulphuric ash 0.1% maximum).

2.c - Chemical agent for oxidation of the substrate

In the absence of indications to the contrary, sodium tetrahydrate perborate (NaBO<sub>3</sub>, 4 H<sub>2</sub>O) at 2 g/l is used as chemical agent for oxidation of the zinc. Oxygenated water (or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can also be used.

2.d - pH

In the absence of indications to the contrary, the solutions are used at their natural acid pH; any increases in pH are obtained by addition of soda.

2.e - Other components and additives

Metal cations may also be added: Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, (rare earths)<sup>n+</sup>.

3) Standard mode of operation for treatment with conversion baths

Table I

Ref.	Step	Composition of the bath	Temperature	Residence time
1	Degreasing	Ridoline™ 1.8% + Ridosol™ 0.18%	55°C	240 s
2	Degreasing	Ridoline™ 0.4% + Ridosol™ 0.04%	55°C	240 s
3	Washing	Running water	25°C	90 s
4	Refining pre-treatment	Fixodine™ 50CF : 0.5 g/l in permuted water	25°C	60 s
5	Conversion treatment	variable	25°C	variable
6	Washing	Running water	25°C	60 s
7	Drying	Pulsed air	80°C	300 s

Ridoline™ is a degreasing aqueous solution containing salts of alkaline metals, surfactants and potassium hydroxide.

Ridosol™ is a wetting base for liquid degreaser comprising a mixture of surfactants.

Fixodine™ 50CF is an activator (also called a nucleator) comprising compounds based on salts of alkaline metals such as titanium salts.

**METHODS of evaluation of the conversion coatings obtained:**

1) Weight per unit area of the deposited coating

In order to determine the weight per unit area, the conversion coating formed on a specific surface is dissolved with a complexing solution, the duration of soaking in this solution being adapted in order to obtain complete dissolution of the coating (of the order of one minute for a coating produced from HC<sub>7</sub>, in a proportion of 0.3 mg/cm<sup>2</sup>).

The weight per unit area, expressed in mg per cm<sup>2</sup>, is evaluated on the basis of the difference in weight between the coated sample and the same sample after being subjected to the dissolution treatment.

The composition of this dissolution solution is as follows:

- disodium salt of EDTA (ethylene diamine tetraacetic acid) : 0.1 M
- MBT (mercaptobenzothiazole) or BZT (benzotriazole) : 0.1 g/l. These compounds limit the dissolution of the metal substrate.

The pH of this solution is adjusted to a value close to 8 by addition of soda in order to obtain optimum complexing of the metal cation.

## 2) Resistance to aqueous corrosion

This test consists of periodic potentiometric measurement of the polarisation resistance  $R_p$  by a voltage sweep of an amplitude of +/- 10 mV around the corrosion potential  $E_{cor}$ .

The device used for this evaluation conventionally includes:

- a tank made from polymethyl methacrylate, the base of which is pierced with a window, and which contains the standard aqueous electrolyte ASTM D1384-87. This electrolyte comprises 148 mg/l of sodium sulphate ( $Na_2SO_4$ ), 138 mg/l of sodium bicarbonate ( $NaHCO_3$ ), and 165 mg/l of sodium chloride ( $NaCl$ ) and has a pH close to 8;
- three electrodes immersed in the electrolyte: a working electrode constituted by the metal surface coated with the conversion coating to be evaluated obstructing the window at the base of the cell, a saturated calomel reference electrode ("SCE"), and a platinum electrode as an auxiliary backing electrode;
- a potentiostat of the Princeton™ 273 or 263 type connected to the three electrodes and controlled by software reference m352 from EG&G Princeton™.

## 3) Resistance to atmospheric corrosion according to the standard DIN 51160

The samples of metal surface are stored in a first time in a humid atmosphere in a humidothermal chamber regulated according to successive cycles, each cycle having the following characteristics:

- first part: duration: 8 hours - 40°C; 100% relative humidity;
- second part: duration: 16 hours – ambient temperature and humidity.

Unless indicated to the contrary, the method then consists of keeping account of the number of cycles after which it is noted that at least 10% of the treated surface is covered with white rust.

#### 4) Behaviour under friction

This test consists of measuring the coefficient of plane-plane friction by increasing the clamping pressure to 80 MPa.

Before the test the treated samples are covered with an oil referenced 6130 from QUAKER, the quantity of oil deposited being of the order to 1 to 2 g/m<sup>2</sup> for example.

#### 5) Behaviour during stamping

This test consists of producing complete stampings from samples of sheet metal blank which have been subjected to the conversion treatment. Thus with an initial blank of 64 mm diameter a dish of 32 mm diameter and 25 mm depth is produced.

On the same type of sheet metal blank on which it is wished to test the surface treatment, the maximum stamping force beyond which rupture of the blank occurs in the course of stamping is evaluated for a predetermined clamping force of the blank holders. This maximum value is recorded for a series of values of the clamping force of the blank holders in such a way as to trace, as illustrated in Figure 1, curves which represent the variation in the maximum stamping force  $F_{max}$  as a function of the force of the blank holder.

6) Suitability for phosphating after degreasing of the coating

In a first time the surface bearing a conversion coating is degreased according to the mode of operation specified in Table I – Steps 1 and 2 of Part 3) "Standard mode of operation for treatment with conversion baths" of "MATERIALS for obtaining the conversion coatings" – in order to eliminate the conversion coating, then a conventional phosphating treatment is carried out on this degreased surface by applying thereto an aqueous composition comprising:

- 2% by volume of Granodine 9580 M/CF (phosphating mixture containing from 10 to 25% of phosphoric acid as well as a small quantity of hydrofluoric acid),
- 0.7% by volume of Starter 958/CF (aqueous solution containing zinc salts in the presence of a slight excess of nitric acid),
- 0.04% by volume of Intensifier No. 1 (aqueous solution of metal salts in the presence of a small quantity of phosphoric acid),
- 0.5% by volume of Primaire M (aqueous solution containing sodium hydroxide > 2%) in order to regulate the pH,
- 0.05% by volume of Compensateur M (aqueous solution based on sodium nitrite, accelerator for crystalline phosphating bath),
- Operating conditions:
  - demineralised water
  - treatment to soaking 2 min
  - temperature = 55°C +/- 2°C
- Control of the bath by chemical analysis:

The analyses should be situated within the following ranges:

  - $[Zn^{2+}] = 0.9$  to  $1.1$  g/l
  - $[Mn^{2+}] = 0.7$  to  $0.9$  g/l
  - $[Ni^{2+}] = 0.18$  to  $0.25$  g/l
  - $[F^-] = 0.25$  to  $0.35$  g/l

In a second time the quality of the phosphating coating obtained is examined with an electron microscope.

7) Suitability for organic coating by cataphoresis after degreasing and phosphating

In a first time the surface treated according to the mode of operation specified in Table I – Steps 1 and 2 of Part 3) "Standard mode of operation for treatment with conversion baths" of "MATERIALS for obtaining the conversion coatings" above – is degreased in order to eliminate the conversion coating, then on this degreased surface a phosphating treatment is carried out according to the mode of operation specified in 6) above. Finally, in a conventional manner an organic coating is deposited by cataphoresis on the phosphated surface according to the following conditions (example of the formulation PPG 752 – 965 1):

- Formula of the control bath:
  - 43.16% by weight of deionised water (10 $\mu$ S maxi),
  - 48.18% by weight of binder derived from polyamine urethanes,
  - 8.66% by weight of paste (dispersion of pigments) for paint by cationic electrodeposition,

With:

- dry extract = 20 – 24%
- pH = 5.7 to 6.1 (at 25°C)
- conductivity of the mixture = 1500 – 2000 mS (at 25°C)
- Conditions of application:
  - temperature of the bath = 28 to 35°C
  - application time = 120 to 180 s
  - anode/cathode ratio = 1 / 4
  - working voltage = 200 – 320 V
  - nominal stoving (T° level) = 15 min at 175°C
  - intended thickness = 18 to 24  $\mu$ m

Example 1

The aim of this example is to determine the conditions of carboxylation treatment according to the invention making it possible to obtain, on a zinc-coated sheet metal surface, a conversion coating which is both compact and finely crystallised.

The treatment of the zinc-coated sheets of steel proceeds according to the following steps:

- preparation of the surface to be treated,
- soaking of the surface prepared in the conversion bath,
- drying and observation of the treatment coating obtained.

The initial preparation treatment is as mentioned in Table 1 under the successive references 1 to 4. The solvent of the conversion bath is a water/ethanol mixture of which the ratio is adjusted in order totally to solubilise the organic acid added.

In order to be able to determine the optimum treatment conditions, different parameters are varied.

#### 1.1 pH

The pH is varied and it is noted that the higher it is the more the conversion coating appears poorly crystallised. Furthermore, a pH which is too high risks resulting in parasitic precipitation of metal hydroxide. This is why in practice the procedure is limited to an acid pH, of between 1 and 7. The minimum value of the pH will be adapted as a function of the metal of the surface in order to ensure a satisfactory deposition of the conversion coating. Thus in the case of zinc the treatment will be effected preferably at a pH of between 4 and 6.

#### 1.2 Temperature of the bath

The temperature of the bath is varied between 20 and 80 °C and it is observed that the increase in the temperature accelerates the speed of deposition.

#### 1.3 Concentration of the organic acid or of the corresponding salt



The concentration of the organic acid is varied and it is noted that the range of concentrations must be between 0.1 and 1.5 M. In fact, as has been seen previously, if the concentration is lower than 0.1M the speed of formation of the conversion coating based on metal carboxylate is no longer sufficient in order to obtain a conversion coating which is effective in the time allowed for the treatment. A concentration higher than 1.5M is not possible because of the limit of solubility of the organic acid close to 1.4 – 1.5M.

When the organic acid or acids is/are used in the form of salts, it is preferable to use chlorides, nitrates or sulphates at a concentration lower than or equal to 3 g/l.

#### 1.4 Length n of the carbon chain of the organic acid

The length of the carbon chain is varied and it is noted that the longer the carbon chain of the aliphatic acid is (high n), the more the crystals of the coating are fine and the more, in equivalent treatment conditions, the weight of the conversion coating is higher: approximately 1.5 times higher for example when n passes from the value 7 to the value 10.

Furthermore, the compactness of the conversion coating also increases with the length of the aliphatic chain of the carboxylic acid used, as well as the resistance to corrosion provided by this coating.

#### 1.5 Nature and concentration of the oxidising agents

Different oxidants are used, such as dissolved oxygen ( $O_2$ ), nitrites ( $NO_2^-$ ), hydrogen peroxide ( $H_2O_2$ ) or perborates ( $BO_3^-$ ). It is noted that the presence of oxidant or accelerating agent has a favourable effect on the compactness of the conversion coating.

#### 1.6 Duration of immersion in the bath or duration of the treatment

The zinc-coated surface to be treated is immersed for several minutes in a bath having the following characteristics:

- ratio water/alcohol : 1;
- $n = 7$  (heptanoic acid),  $[HC_7] = 50 \text{ g/l}$ ,
- oxidising agent: sodium perborate  $NaBO_3 \cdot 4 H_2O$ : 2 g/l;
- $pH \approx 4.7$ .

The duration of treatment is varied and the weight per unit area of the carboxylation coating obtained is observed.

Table II

Immersion time (min.)	0.5	3	5	10
Weight per unit area ( $g/m^2$ )	1	2.4	3.1	3.2

It is noted that the increase in the immersion time in the bath is favourable to the compactness of the coating.

Example 2 – Comparison with the prior art

At the same time the following treatments are carried out on blanks of the same zinc-coated metal sheet under the conditions indicated below.

1. Phosphated metal sheet bearing a coating of which the weight per unit area is of the order of several  $g/m^2$ .

The conventional phosphating treatment is carried out on a degreased surface according to the bath conditions specified in 6) (Suitability for phosphating after degreasing of the coating),

2. Pre-phosphated metal sheet bearing a coating of which the weight per unit area is of the order of 1  $g/m^2$ .

The pre-phosphating treatment is carried out on a degreased surface according to the following conditions:

- conversion bath composed of phosphoric acid, of Mn and of Ni (formulation Chemetall VP 10118, for example)
- drying at 200 °C,
- weight per unit area = 1.1 to 1.5 g/m<sup>2</sup>.

3. Metal sheet oxalated according to FR 2 465 008: the procedure is in accordance with the mode of operation described in example 4 of this document with the aid of a treatment solution containing a complex fluoride and an oxalate.

4. Metal sheet carboxylated according to WO95/21177: the procedure is in accordance with the mode of operation described in example 1 of this document with the aid of a treatment solution containing gallic acid and 3-glycidoxypyril-trimethoxy-silane.

By proceeding with the evaluations of the different types of conversion coatings as defined above in points 3, 4, 5, 6 and 7 of the METHODS paragraph, the following results are obtained:

#### 2.1 Resistance to atmospheric corrosion

Sample tested	Number of cycles
Zinc-coated metal sheet without conversion treatment – oiled QUAKER 2130	10
Pre-phosphated metal sheet – not oiled	20
Metal sheet oxalated according to FR 2 465 008	4
Metal sheet carboxylated according to WO95/21277	7
Metal sheet treated according to the invention (with HC <sub>7</sub> ): 9 min – not oiled	23
Metal sheet treated according to the invention (with HC <sub>7</sub> ): 2 min – not oiled	24
Metal sheet treated according to the invention (with HC <sub>7</sub> ): 2 min + washing –	27

not oiled	
Metal sheet treated according to the invention (with HC <sub>7</sub> ): 5 min – not oiled	25

It will be seen that the treatment according to the invention provides a better resistance to atmospheric corrosion than the treatments according to the prior art.

## 2.2 Behaviour under friction

Type of treatment before oiling	Weight per unit area (g/m <sup>2</sup> )	Coefficient of friction			Comments
		max.	min.	average	
None	0			0.13	High jarring increasing with clamping pressure
Pre-phosphating	1.5	0.19	0.17	0.11	No jarring
FR 2 465 008				0.11	Low jarring
WO95/21277				0.12	Average jarring
Invention: HC <sub>7</sub>	1.2	0.09	0.05	0.07	Very little jarring
Invention: HC <sub>7</sub>	5	0.09	0.04	0.05	No jarring
Invention: HC <sub>10</sub>	5	0.09	0.04	0.05	No jarring

Therefore the conversion treatments according to the invention carried out before oiling make it possible to eliminate the jarring and then a continuous decrease in the coefficient of friction is observed when the clamping pressure increases.

It is also noted that the treatment according to the invention makes it possible to obtain coefficients of friction which are markedly improved relative to the pre-phosphating treatment.

## 2.3 Behaviour during stamping

Figure 1 illustrates the results obtained:

- on the one hand on the metal sheets carboxylated (duration: 5 min) according to the invention: gradients marked by the symbols  $\Delta$  without complementary oiling and by the symbols  $\square$  with complementary oiling with the aid of the oil referenced 6130 from QUAKER;
- on the other hand on the same metal sheets which have not been treated: comparative example represented by the gradients marked by the symbols  $\diamond$ .

In general, the more the gradients obtained are low and not very inclined, the better the behaviour during stamping.

From these three series of tests it is deduced that the conversion treatment according to the invention can advantageously replace the conventional pre-phosphating treatment, all the more so as it avoids the problems of pollution posed by the use of phosphates.

### Example 3. Suitability for painting

The metal surfaces subjected to the conversion treatment according to the invention are used principally in the automotive field. Therefore it is important to check that these surfaces, once they are coated, are compatible with the processes usually used in the industry for the painting of the metal sheets, in particular zinc-coated metal sheets.

#### 3.1 Suitability for degreasing

Shaping by stamping generally necessitates oiling of the metal surface which, when it is wished then to proceed with other operations such as painting or enamelling, requires the elimination of all traces of oil from this surface and, at the same time, the elimination of any conversion coating formed before shaping. For this purpose a degreasing process is carried out, for the success of which it is important that the conversion coating should be easily

eliminated. It is therefore important to check that the conversion coating according to the invention is easily degreaseable.

In a first time, alkaline degreasing of the metal surface bearing a conversion coating is carried out under the conditions specified in Table I – Steps 1 and 2 of Part 3) "Standard mode of operation for treatment with conversion baths" of "MATERIALS for obtaining the conversion coatings".

In a second time the surface of the samples treated and then degreased is observed in order to see whether the conversion coating has disappeared.

The complete disappearance of the carboxylation coating according to the invention is noted.

### 3.2 Suitability for phosphating after degreasing

The procedure according to the mode of operation defined in point 6) of the METHODS is carried out by treating the two faces of the sample according to the invention, namely the bare steel face and the zinc-coated face, and it is observed that the conversion coating appears to give coverage.

### 3.3 Suitability for organic coating by cataphoresis after degreasing and phosphating

The observation of the samples treated according to the invention, degreased, phosphated then coated, does not reveal any particular defect.

### Example 4 – Influence of the co-solvent and the immersion time on the weight per unit area of the conversion coating

The procedure is carried out as described in the MATERIALS and METHODS paragraphs, using heptanoic acid at a concentration of 0.38 mole/litre.

After the application of the conversion treatment, a refining pre-treatment is applied.

As shown in Figure 2, the weight per unit area of the conversion coating is evaluated as a function of the time during which the sheet metal blank to be treated is immersed in the solution according to the invention, for different compositions of solvents (% by volume):

- . Case 1: 62% water, 38% ethanol (symbol +),
- . Case 2: 61% water, 39% 1-propanol (symbol x),
- . Case 3: 43% water, 57% DMSO (symbol Δ),
- . Case 4: 56% water, 44% NMP (symbol □),
- . Case 5: 60% water, 40% diacetone alcohol (symbol ○).

The above mixtures are optimised for maximum solubilisation of the heptanoic acid at more than 95%.

It may be deduced from the curves obtained that:

- the increase profiles of the conversion coating are similar in cases 1, 4 and 5,
- for immersion times less than 280 s, the speed of increase in the coating is lower in cases 2 and 3 than in cases 1, 4 and 5.

On the basis of observations with a scanning electron microscope it is noted that the morphologies of the crystals of the coatings are identical:

- after 30 s of treatment in cases 1, 4 and 5,
- after 300 s of treatment in cases 1, 3 and 4.

Other co-solvents could be envisaged in order to implement the invention, notably amide solvents such as N-methylformamide, N-N-dimethylformamide or sulphone solvents such as tetramethylsulphone.

#### Example 5 – Emulsion in the conversion treatment solution

In order to avoid the use of solvents which may pose safety problems, it is possible to obtain the treatment solutions highly concentrated in organic acid according to the invention with the aid of adapted surfactants.

With the aid of 1% by volume of the product FORAFAC 1033 D from ATOFINA which is an anionic surfactant perfluorinated at 30% in water, from the family of perfluoroalkylsulphonic acid, an emulsion is prepared which contains 50 g/l of heptanoic acid and 2 g/l of sodium tetrahydrate perborate. The emulsion does not contain any solvent other than water and, by virtue of the surfactant, all of the acid is in emulsion and/or solution in the water.

Two treatment solutions are prepared which differ by their pH: one at natural pH  $\approx 4$ , the other at pH adjusted to approximately 4.7 by the addition of soda.

The procedure according to the mode of operation of the METHODS paragraph is carried out by soaking for five minutes of the samples of metal sheets identical to those of Example 3 in one or the other treatment solution, then the treated surface is washed and dried.

According to the observations made on the treated surfaces:

- at pH  $\approx 4$  a carboxylation deposition of  $0.3 \text{ mg/cm}^2$  is obtained which is comparable to those obtained in Example 4 for the same immersion time; the deposit appears to contain traces of the surfactant, which shows that this agent is not passive with regard to the precipitation reaction;
- at pH  $\approx 4.7$  the weight per unit area obtained is a little lower (- 30% approximately) but the morphology of the deposit is comparable to those obtained in Example 4; the deposit no longer contains traces of surfactant.

#### Example 6 – Carboxylation under electrochemical oxidation of the substrate

It is a matter here of producing the metal cations produced from the metal surface by electrochemical means. The substrate, which in this case is a zinc-coated metal sheet, is subjected to a potential and to an anodic current by immersion of the zinc-coated metal sheet



in the treatment solution between two titanium plates which are connected electrically and at the same potential.

As treatment solution a solution of 50% water / 50% ethanol is used containing 0.38 mole/litre of heptanoic acid and of which the pH is between 3.2 and 4.7 according to the quantity of soda added.

The mode of operation described in point 3) of the MATERIALS paragraph is applied; the conversion treatment according to the invention is applied by soaking the sample of metal sheet in the treatment solution and by causing an electric current to pass between the immersed metal sheet and the titanium plates. The procedure is carried out at current densities of 10 and 25 mA/cm<sup>2</sup> for treatment times of 1, 3, 5 and 10 seconds.

Figure 3 represents the results obtained in terms of weight per unit area, the symbol □ representing the curve obtained with a current density of 10 mA/cm<sup>2</sup> and the symbol Δ representing the curve obtained with a current density of 25 mA/cm<sup>2</sup>.

According to these results and from the observations made on the treated surfaces, it is noted that the conversion coatings obtained after 1 to 10 seconds have densities per unit area, morphologies and crystallisations which are comparable to those which are obtained by chemical oxidation after 60 to 300 seconds. This mode of application of the treatment according to the invention permits an improvement by at least a factor of 10 or even 100 in the speed of formation of the conversion coating and is therefore particularly advantageous.

These observations are confirmed by the results of tests on resistance to atmospheric corrosion of samples treated under a current density of 25 mA/cm<sup>2</sup> and set out in Table III:

Table III

Duration of treatment in s	1	3	5	10
Number of cycles	2	5	30	30

Example 7 – Mixture of heptanoic acid and decanoic acid

The procedure is carried out as in Example 4, replacing the heptanoic acid at 0.38 mole/litre by an 80/20 mixture (case A) or a 50/50 mixture (case B) of heptanoic acid (abbreviation: HC<sub>7</sub>) and decanoic acid (abbreviation HV<sub>10</sub>), the immersion time being 5 minutes.

The resistance to atmospheric corrosion of the samples obtained is evaluated according to the test in the METHODS paragraph.

Table IV

Composition of the mixture of acids in %		Weight per unit area (mg/cm <sup>2</sup> )	Number of cycles
HC <sub>7</sub>	HC <sub>10</sub>		
100	0	0.30	25
80	20	0.30	50
50	50	0.32	50
0	100	0.45	50*

\* note the presence after 5 cycles of marks not attributable to white rust.

The resistance to aqueous corrosion is then evaluated by measurements of polarisation resistance of which the results are presented in Figure 4, in which

- the untreated zinc-coated surface is represented by the symbols +,
- the zinc-coated surface treated according to the invention without post-treatment with:
  - heptanoic acid is represented by the symbols Δ,
  - decanoic acid is represented by the symbols x,
  - a mixture of heptanoic and decanoic acids in a ratio HC<sub>7</sub>/HC<sub>10</sub> equal to 80/80 by mole is represented by the symbols \*.

The other gradients of Figure 4 will be dealt with below.

It is noted on comparison of these three gradients that the mixture of heptanoic and decanoic acids has a resistance to aqueous corrosion which is improved relative to heptanoic or decanoic acids used alone.

Observations made on the deposits obtained enable it to be seen that the deposit corresponding to the solution of case B (50/50) has a morphology very different from that obtained with only one of the heptanoic or decanoic acids. The conversion coating obtained with this mixture of acids appears much denser, which would explain the improvement in the resistance to aqueous corrosion. This effect is even more marked in case A (8/20). XR diffractograms of the coating obtained in these two cases demonstrate not only the presence of zinc decanoate but also that of a mixed species.

#### Example 8 – Post-treatments

It is common to effect a post-treatment in order to improve the properties of a conversion coating and the present inventors have therefore sought to determine the type of post-treatment which is best adapted to the substrates bearing a conversion coating according to the invention.

A zinc-coated metal sheet is treated by soaking for five minutes in a 50/50 water/ethanol solution containing 0.38 mole/litre of heptanoic acid and 2 g/l of sodium hydrate perborate.

The post-treatment is then effected by soaking in a post-treatment solution, the characteristics of which are set out in Table V, for 60 seconds, before the final washing of the mode of operation described in point 3 of the MATERIALS paragraph.

Table V – Post-treatment solutions

Test	Ref.	Company	Composition	Concentration	pH
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Si (1)	44,016-7	ALDRICH	3-glycodoxypropyl-trimethoxysilane	5 g/l	4.7
Ti	30,838.2	FLUKA	K <sub>2</sub> TiF <sub>6</sub>	3.7 g/l	3.4
Gd <sup>III</sup>	19914-0250	ACROS	Gd(NO <sub>3</sub> ) <sub>3</sub> , 5 H <sub>2</sub> O	0.01 M	4.7
Lu <sup>III</sup>			Lu(NO <sub>3</sub> ) <sub>3</sub>	0.01 M	4.7

(1) solution comprising 10% of methanol by weight

Once the post-treatment has been carried out, the treated surface of the samples is observed and/or analysed and a potentiometric evaluation of the resistance to aqueous corrosion is carried out according to point 2 of the MATERIALS paragraph.

It is noted that the Ti post-treatment has no influence but that the Si post-treatment permits a slight improvement in the resistance to corrosion, apparently without morphological modification of the conversion coating.

In the case of post-treatment solutions containing rare earth metals in the +3 oxidation state (Gd<sup>III</sup>, Lu<sup>III</sup>), tested at the same concentration and at the same pH, a deposit of rare earths on the conversion coating is observed, but the effect of this deposit on the polarisation resistance  $R_p$  is different according to the nature of the lanthanide, as illustrated in Figure 4: significant effect in the case of Lu<sup>III</sup>, very substantial effect in the case of Gd<sup>III</sup>.

In conclusion, amongst the post-treatment solutions evaluated, it is the solution of Gd<sup>III</sup> which seems to have the greatest influence on the morphology of the carboxylation coating and on the resistance to aqueous corrosion which it provides. It also makes it possible to increase the resistance to atmospheric corrosion since an improvement of approximately 10 cycles is observed during tests carried out in a humidothermal chamber.

#### Example 9 – Addition of gadolinium ions to the treatment solution

At point 2 e) of the MATERIALS paragraph, it is indicated that other components or additives may be introduced into the carboxylation solution according to the invention. In the

preceding example the effect of certain compounds was evaluated at the level of a post-treatment operation, and now the effect of these same compounds will be evaluated at the level of the treatment itself, using these compounds as additive in the conversion solution.

The treatment according to the invention is carried out by soaking for five minutes in a 50/50 water/ethanol solution containing 0.38 mole/litre of heptanoic acid, 2 g/l of sodium hydrate perborate, and one of the additives listed in Table VI, whereby the pH can be adjusted by the addition of nitric acid

The mode of operation described in point 3 of the MATERIALS paragraph can be applied without carrying out post-treatment.

Table VI – Treatment additives

Test	Ref.	Company	Composition	Concentration	pH
Si (1)	44,016-7	ALDRICH	3-glycodoxypropyl-trimethoxysilane	5 g/l	4.8
Ti	30,838.2	FLUKA	K <sub>2</sub> TiF <sub>6</sub>	3.7 g/l	4.5
Gd <sup>III</sup>	19914-0250	ACROS	Gd(NO <sub>3</sub> ) <sub>3</sub> , 5 H <sub>2</sub> O	0.01 M	3.5
Gd <sup>III</sup>	idem	idem	idem	0.01 M	4.7

1) solution comprising 10% of methanol by weight;

After observation and analysis of the treated surface of the samples, it is noted that the case Ti has a negative effect on the carboxylation reaction, whilst the cases Si and Gd<sup>III</sup> at pH=4.7 do not permit any difference to be observed relative to carboxylation without additives.

On the other hand, the case Gd<sup>III</sup> at pH=3.5 gives a conversion coating composed of two types of crystals of different composition and probably of different shapes. The appearance of this structure is observed for a pH higher than 4. By carrying out the polarisation measurements according to point 2 of the METHODS paragraph, values of R<sub>p</sub> are obtained which are

approximately 5 times higher than those obtained on the standard sample obtained by carboxylation treatment without additive.